

Original Research Article

Advances of Membrane Technology in Acid Gas Removal in Industries

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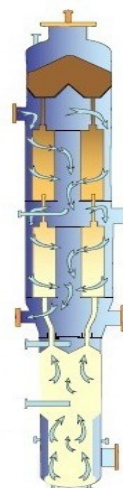
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ABSTRACT

The presence of H₂S and CO₂ is unfavorable in many processes and flows, particularly in natural gas flows. Therefore, removing this gas is one of the important issues in many systems. One of the most widely used techniques is the use of membrane. Therefore, the gas that passes through the membrane has low pressure. Membrane system is used to absorb a high volume of CO₂. The factors needed for this kind of separation include gas composition, pressure, and temperature difference. An enhanced electrochemical membrane can also be used with coal gas to separate acid gases. Hydrogen is so rich in this process in which cathode and sulphur steam are produced and then exited. Granular activated carbon (GAC) can be used as supporting material to absorb H₂S. The advantages of this method are including high capacity for H₂S absorption and gas emission. Removing the H₂S from waste gases or natural gas with high densities is done via bio-filter in this system. Granular activated carbon can be used as a supporting material to stabilize the microorganisms. Principal properties of the supporting material are including the mass density, the area of special surface, and the amount of its pH. This research discusses the membrane technology in removing the acid gases in the oil technology.

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Introduction

In 1999, Iran with 263 million tons ranked first in CO₂ production in the Middle East (showing a 45.6% increase compared to 1990). Chemical industries in Iran produced 58.4 million tons of the total 263 million tons of this gas [1-4].

Different countries have come up with numerous ways to reduce CO₂ levels as this gas causes accumulation greenhouse gases, increases global temperatures, contributes to sea level rise, and causes droughts and acid rain [5-9].

Many studies have been carried out on increasing CO₂ absorption by using chemical solvents. Specifically, CO₂ absorption by amines is the most common technology employed for this purpose. Since amines of different types have their specific disadvantages when used for CO₂ absorption (e.g. corrosion, low absorptive capacity, high energy requirement for reduction, etc.) [10-16], various studies have been carried out in recent years to upgrade and improve CO₂ absorption by amines. One of these studies is the combination of third type amines with a first or second type amine, the combination of amines with ionic fluids, and the addition of nanoparticles to amines.

Morteza Afkhamipour et al. conducted a laboratory study and modeled CO₂ solubility, density, and viscosity in a 1-Dimethylamino-2-propanol (1DMA2P) solution. The data on equilibrium solubility of CO₂ were predicted using the Deshmukh-Mather thermodynamic model. They also modeled and predicted the experimental data of viscosity based on the Eyring conventional transition state theory and using the Eyring-Wilson and the Eyring-NRTL (non-random two liquid) models. Results showed that the Eyring-Wilson model predicted the experimental data of viscosity better than the Eyring-NRTL model [17].

ADAK S et al. studied CO₂ solubility in an aqueous solution of 2-Diehtylaminoethanol+ Piperazine in the pressure range 0.1-65 kPa and temperature range 303.15-323.15 K. They developed a thermodynamic model that could relate

the experimental data to CO₂ solubility extremely well. The experimental data of density were fitted to the Redlich-Kister, Grunberg-Nissan, Gonzalez-Olmos and Iglesias equations and the data on viscosity to the Grunberg-Nissan model. Results of the experiments showed that the DEAE+PZ combination absorbed CO₂ better and in greater quantities than the MDEA+PZ combination [18].

Bikash Kumar Mondal et al. investigated equilibrium solubility and enthalpy of CO₂ absorption in aqueous bis (3-aminopropyl) amine solution and its mixture with MEA, MDEA, AMP, and K₂CO₃. They noticed that the DPTA+K₂CO₃ mixture offered the most favorable loading capacity, enthalpy and viscosity among the mixed solvents. Although solid loading in CO₂ was 0.8 at 40°C, it was accompanied by the high pressure resulting from CO₂ (3kPa) [19].

Helei Liu et al. analyzed CO₂ solubility and absorption rate in aqueous solutions of 1-Diethylamino-2-propanol (1DES2P). They investigated performance of CO₂ absorption in the 1DEA₂P solution by taking into account CO₂ equilibrium solubility, absorption rate, and absorption heat, and reported that 1DEA₂P could be considered an alternative solvent for CO₂ absorption [20].

Hossein Shahraki et al. studied CO₂ solubility in absorption and desorption processes with the solvent methyl di-ethanolamine (MDEH) activated with Piperazine and reinforced by NPs at 12, 25, 50, and 100 ppm. CO₂ solubility was investigated at 40 and 120°C. The experiments were conducted at CO₂ partial pressure of 0.1-26 atm. They reported that the solvent CO₂ loading was enhanced by almost 37.5% through introducing the NPs at 25 ppm. Therefore, the process in which NPs were added demonstrated a higher productivity and cost-effectiveness [21].

Jiazong Jiang et al. conducted a laboratory study on the effects of NPs on CO₂ absorption by applying aqueous solutions of MEA and MDEA in a bubble column reactor. They studied the effects of various factors influencing CO₂

absorption including loading solid NPs, NP size and type, total volume flow rate of the mixed gas, and the initial CO₂ mass fraction. Results indicated that most NP types considerably increased CO₂ absorption except for nanoparticles such as SiO₂ NPs. Moreover, CO₂ absorption in MDEA-based Nano fluids varied based on the different NPs following this order: TiO₂ > MgO > Al₂O₃ > SiO₂ [22].

Recent research has revealed that solvent DEEA is capable of absorbing CO₂. At certain concentrations, NPs can increase solubility of CO₂ in amine solvents. TiO₂ NPs have desirably increased solubility of CO₂. Therefore, the present study examines discontinuous absorption of CO₂ in DEEA in a laboratory system to measure the volume of CO₂ absorption in solvents. The research variables include solvent concentration, initial pressure, and concentration of TiO₂ NPs. Thermodynamic studies will then be carried out on the data, response surface methodology will be employed in designing the experiments, and results will be analyzed using the Design-Expert software.

In this present study various processes based on hydrogen sulfide and other acidic gases such as carbon dioxide, carbon disulfide, mercaptans, and carbonyl sulfide have been introduced for natural gas sweetening. One of these processes involves the use of solvents. Also a device that measures solubility of gases in liquids will be employed to measure solubility of CO₂ in solvent DEEA in the presence of TiO₂ at different solvent concentrations (10, 15, 20% w/w), various pressures (5, 10, and 15bar) and different TiO₂ concentrations (0.05 and 0.1% w/w) at ambient temperature.

Theory

As is well known, CO₂ absorption into an amine solution combines both physical and chemical absorptions. In order to obtain the CO₂ equilibrium solubility, the concentration of CO₂ in the aqueous solution needs to be calculated.

An equation of state (EOS) is required to perform calculations related to solubility, for which the present study employed the Peng-Robinson EOS (1). The parameters of this equation, proposed in 1967 by Peng-Robinson, are obtained by using the critical properties and the acentric factor [23].

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \quad (1)$$

The EOS must be rewritten in terms of the compressibility coefficient Z to perform the calculations. Equation 2 is obtained in terms of Z by using the Peng-Robinson EOS.

$$Z^3 - (1-B) Z^2 + (A-2B-3B) Z - (AB-B^2 - B^3) = 0 \quad (2)$$

$$A = \frac{aaP}{R^2 T^2} \quad (3)$$

$$B = \frac{bP}{RT} \quad (4)$$

$$a = 0.457235 \frac{(RT_c)^2}{P_c} \quad (5)$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (6)$$

$$\alpha = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2) (1 + T_r^{0.5})]^2 \quad (7)$$

$$T_r = \frac{T}{T_c} \quad (8)$$

In the above equations, V is the molar volume, T_c and P_c are the temperature and pressure at the critical point, respectively, R denotes the gas constant, and ω is the acentric factor. By solving Equation 2 in vapor-liquid

equilibrium calculations, the largest obtained value for Z is used for the vapor phase and the smallest for the liquid phase. Using the values of Z obtained at the initial and equilibrium (final) temperature and pressure, the numbers of the initial and final (equilibrium) moles are determined from Equations 9 and 10:

$$n_0 = \frac{P_0 V_0}{Z_0 R T_0} \tag{9}$$

$$n_e = \frac{P_e V_e}{Z_e R T_e} \tag{10}$$

$$\Delta n = n_0 - n_e \tag{11}$$

$$x = \frac{\text{Mole Absorber}}{\text{Solvent kg}} \tag{12}$$

$$x = \frac{\text{Standard Volume}}{\text{Volume of Solvent cm}^3} \tag{13}$$

Equation 12 defines solubility in terms of the number of carbon moles in CO₂ per kilogram of the solvent. To calculate the number of moles of solute for CO₂ dissolved in the solvent, the volumetric method is employed using Equation 13, in which the standard volume is calculated from the following equation:

$$V_{STP} = \frac{nRT}{P} \tag{14}$$

In Equation 14, the volume of the carbon dioxide gas is calculated under standard conditions (pressure of 1 atm and temperature of 25°C).

Experimental

The experiments were performed using a stainless-steel jacketed reactor (SS-316) with an internal volume of 296 cm³ and a pressure endurance of 200 bars. The internal vessel was equipped with four valves with a pressure endurance of 6000 psi, of which two were ball valves used to inject the solution and drain the water/gas mixture the test, and two were needle valves, one of which was used for gas injection, and the other for connecting to the gas chromatograph and gas sampling. There is also a gas loading chamber with a volume of 1820 cm³, which is fitted with two ball valves for gas injection and another for discharging into the reactor. A platinum temperature sensor (Pt-100) with a precision of ±0.1 K was used to measure the reactor internal temperature. The tank pressure was measured with a BD sensor with a precision of about 0.01 MPa. A swing mixer was used for to proper mixing in the hydrate formation main tank, and a pump was used to create vacuum inside the cell. The apparatus used in this study is schematically shown in Fig. 1.

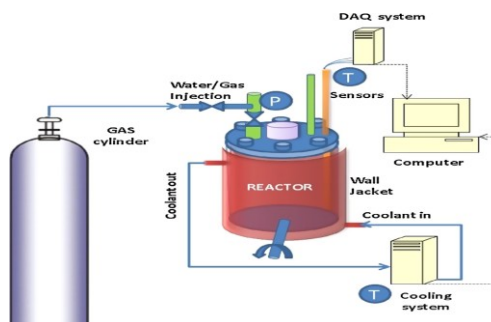


Figure 1. Schematic view of the apparatus

Material

Materials used in this work include: Carbon dioxide gas was purchased from the Arvand Industrial Company of gases and with a purity of 99.99%. **The carbon dioxide gas capsule is 50 liters in volume and has an initial pressure of 5 MPa.** Nanoparticle of titanium dioxide as a suspended particle in a solvent and an effect on adsorption in some experiments with TiO₂ chemical formula from Nano Pasargad New Co., Diethyl ethanolamine (2-DEEA) with a purity of 99.99% from the Swiss Folka Company with the chemical formula C₆H₁₅NO and demineralized (DM) Water for solution preparation. **Made from industrial companies.**

Results

In this work, the solubility of carbon dioxide in DEEA solution was measured with/without of titanium dioxide nanoparticle with various concentrations and pressures, so the experimental results are presented in this section.

Investigation of carbon dioxide solubility using the Peng-Robinson equation

To study the actual solubility behavior of CO₂ in DEEA, its solubility was calculated and investigated by using the Peng-Robinson EOS. Results obtained from these calculations are presented in Table 1.

Table 1. Solubility of carbon dioxide using the Peng-Robinson equation

RUN	Solvent(AMIN)	Nano particle	P ₀	V(STP)	X
1	20	0	9	4239.28	42.39
2	15	0	13.5	3265.69	32.66
3	15	0	4.5	3242.89	32.43
4	10	0	9	2581.36	25.81

5	20	0.05	13.5	4434.28	44.34
6	20	0.05	4.5	4150.51	41.51
7	15	0.05	9	3764.54	37.65
8	10	0.05	13.5	2640.63	26.41
9	10	0.05	4.5	2282.96	22.83
10	20	0.1	9	4135.96	41.36
11	15	0.1	13.5	3668.65	36.69
12	15	0.1	4.5	3178.92	31.79
13	10	0.1	9	2506.68	25.07

As shown in Table 1, in the absence of the NPs, solubility of CO₂ in water improves with increases in the concentration of the amine solvent, increasing further if NPs are added to the solution. Changes in solubility in the presence of the NPs and the solvent are now further studied and interpreted by using the Figure s.

The effect of different parameters on solubility

In Figure s 1-6, effects of each parameter (pressure, NP, and solvent) are presented individually or in combination according to what was stated in Table 1.

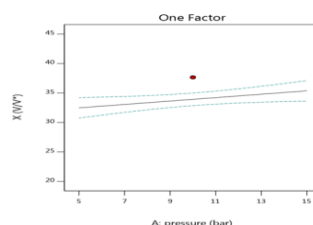


Figure 2. The effect of pressure on solubility

Figure 2 indicates effects of pressure on solubility. Effects of pressure on solubility at NP concentration of 0.05% w/w and solvent concentration of 15% w/w show that solubility of CO₂ is less affected by pressure compared to the solvent type. The reason for this is that higher pressures at constant temperature increase the partial pressure (the pressure exerted on each part of this mixture). Consequently, further gas compression takes place, a larger number of molecules enter the liquid phase, and solubility increases.

The effect of nanoparticle concentration on solubility

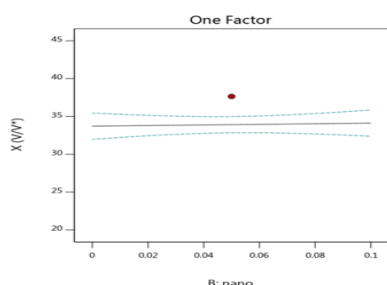


Figure 3. The effect of nanoparticle concentration on solubility

Figure 3 shows the effects of NPs on the solubility of CO₂ at pressure of 10 bar and solvent concentration of 15% w/w. As shown in this Figure, the effects of the NPs are negligible compared to those of the other two parameters (pressure and solvent). In the beginning, as soon as the gas is absorbed by the Nano fluid, the stable NPs break up

the gas bubbles into smaller ones and the mass transfer area increases. Therefore, solubility of small gas bubbles increases eventually, leading to increased total absorption by the Nano fluids.

The effect of amine solution concentration on solubility

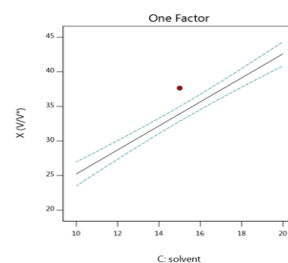


Figure 4. The effect of amine solution concentration on solubility

Figure 4 displays effects of the solvent on carbon dioxide solubility at pressure of 10 bar and NP concentration of 0.05% w/w. It shows that the solute greatly influences solubility of CO₂ compared to the other two parameters (pressure and NPs). We can say that the amine solution decreases the surface tension of the solvent. In other words, accumulation of the amine solution at the interface between immiscible fluids can reduce surface tension. This decreases mass-transfer resistance at the surface, facilitating the penetration of gas CO₂. As a result, the kinetic behavior is improved leading to higher solubility of gas CO₂ in the solvent.

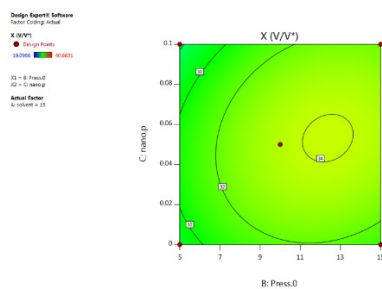


Figure 5. The simultaneous effect of pressure and nanoparticles on solubility

Figure 5 presents simultaneous effects of pressure and NP concentration on solubility of CO₂. This Figure shows that, at the constant solvent concentration of 15%w/w, a combination of pressure in the 5-15 bar range and NP concentration in the 0-0.1% w/w range does not significantly affect solubility of CO₂.

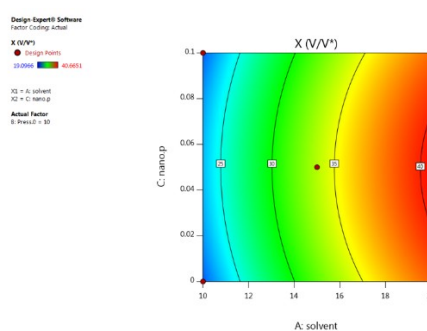


Figure 7. The simultaneous effect of solution and nanoparticles on solubility

Figure 7 shows that, at the pressure of 10 bar, the simultaneous use of the NP concentration range 0-0.1% w/w and the solvent concentration higher than 15% w/w results in the highest solubility percentage.

Conclusion

In the present research, solubility of CO₂ in DEEA in both absence and presence of TiO₂ NPs was studied. The following results were obtained:

All experiments were conducted at a constant temperature. Therefore, effects of temperature were not taken into account in any of the results. In general, the experiments were carried out in 13 stages and at 3 different pressures (5, 10, and 15 bar) to study the degree of solubility of CO₂ in DEEA at concentrations of 10, 15, and 20% w/w of the solvent in both presence and absence of TiO₂ NPs with a concentration range of 0-0.1% w/w. Results indicated that, at constant pressure, increases in the concentration of the DEEA solution increased solubility of CO₂, but increases in the concentrations of the NPs did not considerably change solubility. At constant concentration of the DEEA solution, increases in the pressure of the system improved solubility of CO₂. Moreover, the performed analyses of the Figure s produced by the Design Expert-11 software suggested

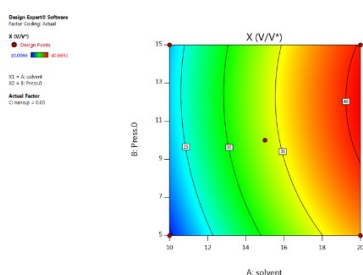


Figure 6. The simultaneous effect of pressure and solvent on solubility

Figure 6 displays that, at NP concentration of 0.05% w/w, the greatest effect on solubility is observed at solvent concentrations higher than 15% w/w and pressure in the 5-15 bar range.

that the DEEA solution was a more influential factor of solubility.

Nomenclature

P, bar	pressure
T, K	Temperature
R, j. mole. k	universal gas constant
v, m ³	volume
Z,	Compressibility factor
T _C , K	Critical temperature
P _C , bar	Critical pressure
T _r ,	Reduced temperature
n ₀ , mole	Initial moles
n _e , mole	Secondary moles

P ₀ , bar	Initial pressure
P _e , bar	Secondary pressure
v ₀ , m ³	Initial volume
v _e , m ³	Secondary volume
T ₀ , K	Initial temperature
T _e , K	Secondary temperature
a,b, A,B	Constant
V _{STP} , m ³	Standard volume
ω	Acentric factor

References: